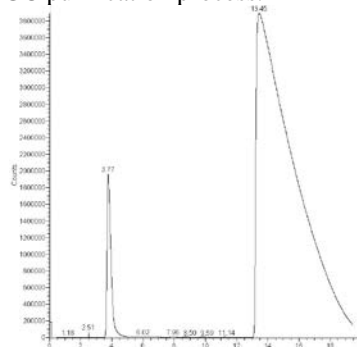


**TWO DISTINCT SECONDARY CARBONATE SPECIES IN OC METEORITES FROM ANTARCTICA ARE POSSIBLE ANALOGS FOR MARS CARBONATES.** M. E. Evans<sup>1,2</sup>, P. B. Niles<sup>2</sup>, D. R. Locke<sup>3</sup>, P. Chapman<sup>1</sup>; (michael.e.evans@nasa.gov) <sup>1</sup>Texas A&M University, College Station, Tx; <sup>2</sup>NASA Johnson Space Center, Houston, Tx; <sup>3</sup>HX5-Jacobs JETS Contract–NASA Johnson Space Center, Houston, Tx.

**Introduction:** Meteorites falling in Antarctica are captured in ice and stored until the glacial flow transports them to the surface where they can be collected. Prior to collection, they are altered during interactions between the rock, the cryosphere, and the hydrosphere. The purpose of this study is to characterize the stable isotope values of terrestrial, secondary carbonate minerals from Ordinary Chondrite (OC) meteorites collected in Antarctica. This facilitates better understanding of terrestrial weathering in martian meteorites as well as mechanisms for weathering in cold, arid environments as an analog to Mars. OC samples were selected for analysis based upon size and collection proximity to known martian meteorites. They were also selected based on petrologic type (3+) such that they were likely to be carbonate-free before falling to Earth [1]

**Methodology:** Four (4) different OCs were analyzed from two Antarctic collection regions. The meteorites analyzed were RBT-04149, RBT-04298, ALH-77214, and ALH-77299. The samples were gently crushed to a size < 750  $\mu\text{m}$ . Each sample of ~0.5g was reacted with 1.5-2.0 ml of  $\text{H}_3\text{PO}_4$  at 30°C and 150°C.  $\text{CO}_2$  was extracted at three different steps: 1) Rx0 after 1 hr. at 30°C; 2) Rx1 after 18 hrs. at 30°C, and 3) Rx2 after 3 hrs. at 150°C. This follows prior stepped extraction techniques [2, 3] but applied to Antarctic OCs.

The extracted  $\text{CO}_2$  was then purified using a TRACE GC with a Restek HaySep Q 80/100 6' 2mm stainless column. Figure 1 demonstrates that substantial other gases were successfully separated from the  $\text{CO}_2$  during the GC purification process.



**Figure 1: Separation of  $\text{CO}_2$  (3.77 min) from other gasses (13.45 min), using GC**

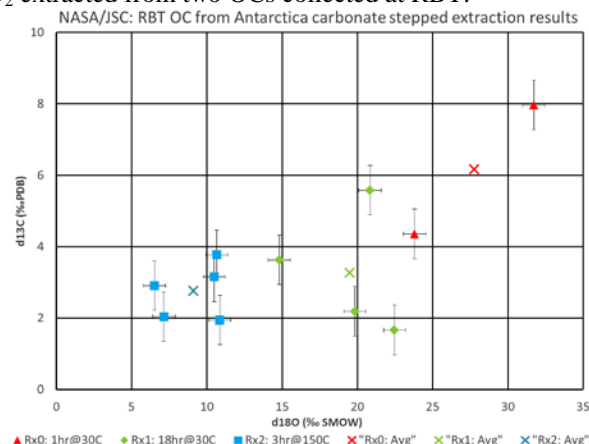
The extraction process was validated using calcite standards of known  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values in 20 test runs reacted at 30°C. All of the calcite standards demonstrated 100% yield following the 18 hours ex-

traction. The  $\text{CO}_2$  isotopic values were then measured using a Thermo MAT 253 IRMS in Dual Inlet mode.

The extraction process was next performed on a Greenland IV siderite reacted at 150°C in 12 test runs to determine its  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. With the known isotopic values of both a calcite and a siderite, specific amounts of each carbonate standard were added to a carbonate-free terrestrial Hawaiian Island Basalt (HIB) to test the stepped extraction technique with a mixed carbonate/silicate sample. Upon completion of 40 test runs the results indicated a  $2\sigma$  error for  $\delta^{13}\text{C} = \pm 0.694\text{‰}$  and  $\delta^{18}\text{O} = \pm 0.738\text{‰}$ .

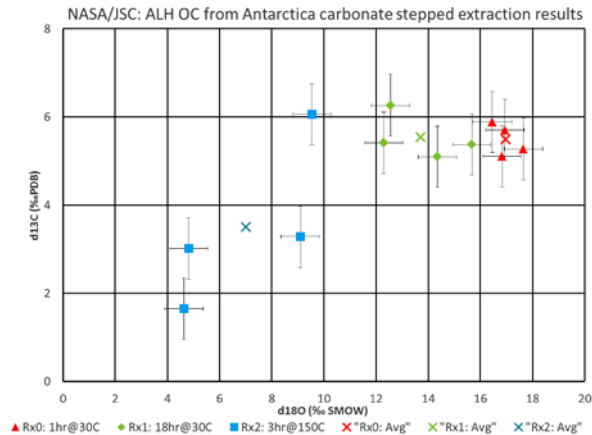
**Results:** The OC analyses yielded  $\text{CO}_2$  that was released in each reaction step at both temperatures. A clear difference in  $\delta^{18}\text{O}$  could be observed between  $\text{CO}_2$  released at 30°C (1 hour and 18 hour reaction time), and  $\text{CO}_2$  released at 150°C (3 hour reaction time). The overall range in  $\delta^{13}\text{C}$  values is small (+2 to +8‰), but  $\delta^{18}\text{O}$  values range from +4‰ to +32‰ with the  $\text{CO}_2$  released in the 150°C step (Rx2) consistently having the lowest  $\delta^{18}\text{O}$  values.

**Discussion:** Results for each Ca-rich extraction (30°C) vary by region in Antarctica where the OC is collected. The RBT site (Roberts Massif) is located at W177°06' S85°32'6" near the Queen Maud range of the Transantarctic Mountains inland towards the South Pole. Figure 2 reflects the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for  $\text{CO}_2$  extracted from two OCs collected at RBT.



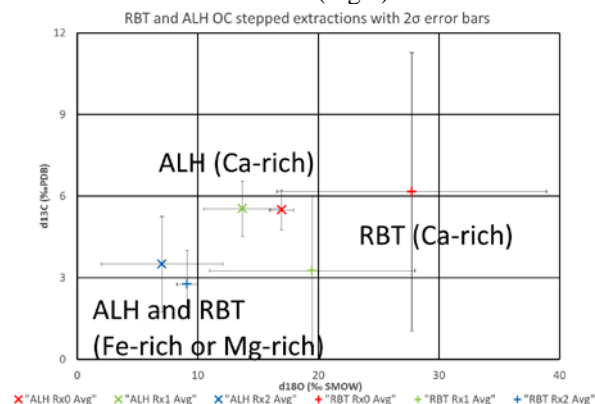
**Figure 2: Results for OC collected from RBT**

The ALH (Allan Hills) site is located approximately 650 miles southeast of the RBT site, near the Scott coast, the Odell Glacier, and the Prince Albert Mountains at approximately E159°06' S76°38'. Figure 3 reflects the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for  $\text{CO}_2$  extracted from two OCs collected at ALH.



**Figure 3: Results for OC collected from ALH**

If the results are averaged and graphed by collection site, then regional differences can be observed. The RBT Ca-rich values are heavier in  $\delta^{18}\text{O}$  than the ALH samples, but it is unclear if there is a regional variability in Ca-rich  $\delta^{13}\text{C}$  due to the large error bars. The Fe-rich/Mg-rich carbonate releases  $\text{CO}_2$  (at  $150^\circ\text{C}$ ) that is lighter in both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  than the  $\text{CO}_2$  from the Ca-rich carbonate, and it does not seem to vary based on collection location (Fig 4).



**Figure 4: Results for OC collected at ALH & RBT**

Prior studies and the data collected in this study show that calcite reaction kinetics will yield 100% of sample  $\text{CO}_2$  after 18 hr at  $30^\circ\text{C}$ , however Fe-rich and Mg-rich carbonates will largely not react [2]. It is thus expected that the the first two reaction steps (Rx0, Rx1) at  $30^\circ\text{C}$  release  $\text{CO}_2$  from Ca-rich carbonates, while the final step (Rx2) would release  $\text{CO}_2$  from either Fe-rich or Mg-rich carbonates. Future analysis of these OC samples using X-Ray Diffraction (XRD) and/or Scanning Electron Microscopy (SEM) will attempt to identify the specific carbonate phases present.

The isotope values measured in this study indicate that two chemically and isotopically distinct secondary carbonate populations exist in these samples. This is a new observation enabled by the use of the stepped analysis technique, performed here for the first time on

these samples. The data are consistent with most of the previously reported data and may now explain some of the variation observed between the studies [4-6].

The carbon isotope values in both populations are consistent with carbonate formation at  $-10^\circ\text{C}$  in equilibrium with atmospheric  $\text{CO}_2$  of  $\delta^{13}\text{C} = -7\text{‰}$  [7], but the  $\delta^{18}\text{O}$  values indicate that the OC carbonate species formed under a wide range of temperatures. All carbonate  $\delta^{18}\text{O}$  values are consistently heavier than what would be expected if formed in equilibrium with melted ice in Antarctica of  $\delta^{18}\text{O} < -40\text{‰}$  [7]. One possible explanation is that the secondary carbonates (especially the Ca-rich carbonates) are not formed in equilibrium with Antarctic melt water, but from atmospheric  $\text{CO}_2$  (with  $\delta^{18}\text{O} \approx +41\text{‰}$  [8] with seasonal and geographic variability of  $< 4\text{‰}$  [9]).

The possibility that these terrestrial, secondary carbonates are atmospherically dominated in both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  suggest that they formed from very small volumes of liquid water, possibly small water films. Atmospheric  $\text{CO}_2$  raises the  $\delta^{18}\text{O}$  of the water film through equilibration. This may be a good analog for carbonate formation on Mars where  $\Delta^{17}\text{O}$  values indicate that the carbonates are atmospherically dominated [10] and where it is likely that liquid water may only exist in small films. Thus, martian carbonates in the martian meteorites may have been formed in a low water-rock ratio formation environment similar to the one experienced by the OCs collected in Antarctica.

**Conclusions:** This data demonstrates that two distinct species (Ca-rich and Fe-rich/Mg-rich) of terrestrial carbonates form on OC meteorites collected in Antarctica, with a regional variation in  $\delta^{18}\text{O}$ . Both the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values suggest atmospheric  $\text{CO}_2$  dominates this carbonate formation, and these Antarctic formation processes could be an analog for carbonate formation on Mars.

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